electronic reprint

Acta Crystallographica Section C

Crystal Structure Communications

ISSN 0108-2701

Editor: **George Ferguson**

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Hydrogen bonding in 1:1 proton-transfer compounds of 5-sulfosalicylic acid with 4-*X*-substituted anilines (*X* = F, Cl or Br)

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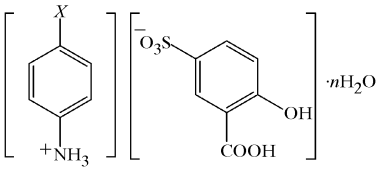
Received 27 October 2004
Accepted 16 December 2004
Online 22 January 2005

The crystal structures of three proton-transfer compounds of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) with 4-*X*-substituted anilines (*X* = F, Cl and Br), namely 4-fluoroanilinium 5-sulfosalicylate (3-carboxy-4-hydroxybenzenesulfonate) monohydrate, $C_6H_7FN^+\cdot C_7H_5O_6S^-\cdot H_2O$, (I), 4-chloroanilinium 5-sulfosalicylate hemihydrate, $C_6H_7ClN^+\cdot C_7H_5O_6S^-\cdot 0.5H_2O$, (II), and 4-bromoanilinium 5-sulfosalicylate monohydrate, $C_6H_7BrN^+\cdot C_7H_5O_6S^-\cdot H_2O$, (III), have been determined. The asymmetric unit in (II) contains two formula units. All three compounds have three-dimensional hydrogen-bonded polymeric structures in which both the water molecule and the carboxylic acid group are involved in structure extension. With both (II) and (III), which are structurally similar, the common cyclic $R_2^2(8)$ dimeric carboxylic acid association is present, whereas in (I), an unusual cyclic $R_3^3(8)$ association involving all three heterospecies is found.

Comment

3-Carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, 5-SSA) has proved a particularly useful synthon for molecular assembly through hydrogen bonding, having, in addition to the primary sulfonic acid functional group, interactive carboxylic acid and phenol substituent groups. In the 5-SSA anion formed in the reaction of 5-SSA with Lewis bases, all of these substituent groups provide hydrogen-bonding donor or acceptor atoms with potential for both primary and secondary structure extension. In a previous study of the proton-transfer compounds of 5-SSA with a series of quinolines (Smith, Wermuth & White, 2004), we reviewed the structural systematics of 5-SSA compounds with Lewis bases, including those with aniline (1:1) (Bakasova *et al.*, 1991), guanidine [both as a 1:1 anhydrate (Zhang *et al.*, 2004) and a 2:1 monohydrate (Smith, Wermuth & Healy, 2004)], theophylline (a 1:1 monohydrate; Madarasz *et al.*, 2002), trimethoprim (a 1:1 dihydrate; Raj *et al.*, 2003) and 4,4′-bipyridine (a 1:2 dihydrate; Muthiah *et al.*, 2003). It was observed that, with the majority of compounds, water was incorporated into the crystal structure and was involved in direct hydrogen-bonding interactions with the aminium groups, whereas with the anhydrous compounds, the primary interaction involved the aminium H atoms and sulfonate O-atom acceptors. In some examples, particularly those with polycyclic heteroaromatic amines (Smith, Wermuth & White, 2004), the structures featured π–π hetero- and homomolecular interactions.



(I) *X*=F; *n*=1
(II) *X*=Cl; *n*=0.5
(III) *X*=Br; *n*=1

The crystal structures reported here are those of 5-SSA with the 4-halo-substituted anilines 4-fluoroaniline (FAN) [*viz.* 4-fluoroanilinium 5-sulfosalicylate monohydrate, $C_6H_7FN^+\cdot C_7H_5O_2S^-\cdot H_2O$, (I)], 4-chloroaniline (CLAN) [4-chloroanilinium 5-sulfosalicylate hemihydrate, $C_6H_7ClN^+\cdot C_7H_5O_2S^-\cdot 0.5H_2O$, (II)] and 4-bromoaniline (BRAN) [4-bromoanilinium 5-sulfosalicylate monohydrate, $C_6H_7BrN^+\cdot C_7H_5O_2S^-\cdot H_2O$, (III)]. Fig. 1 shows the atom-numbering scheme used for the substituted anilinium cation, the 5-sulfosalicylate anion and the water molecule of solvation in (I); the same scheme is employed for (II) and (III), and has previously been employed in 5-SSA structures reported by this group (Smith, Wermuth & Healy, 2004; Smith, Wermuth & White, 2004). Table 4 lists selected bond distances and angles for (I)–(III). All three examples involve proton transfer from the sulfonic acid group to the amine group of the aniline molecule, with subsequent

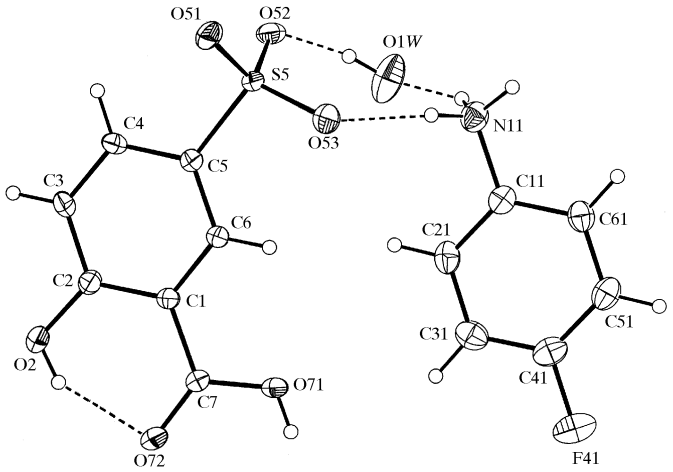


Figure 1
The molecular conformation and atom-numbering scheme for the FAN^+ cation, the $5\text{-}SSA^-$ anion and the water molecule in (I), showing the cyclic $R_3^3(8)$ hydrogen-bonding association. Non-H atoms are shown as 30% probability displacement ellipsoids.

 DOI: 10.1107/S0108270104033451

hydrogen bonding (Tables 1–3) involving also the water molecule, giving in all cases three-dimensional network structures. The hydrogen bonding includes one type not encountered before in 5-SSA Lewis base compounds, namely a rare cyclic $R_3^3(8)$ association in (I), involving both an anilinium $N^+—H\cdots O$(sulfonate) and an anilinium $N^+—H\cdots O$(water) interaction (Fig. 1). There is no occurrence of the anilinium–sulfonate $R_2^2(8)$ dimer interaction commonly found in anhydrous guanidinium sulfonates (Russell *et al.*, 1994; Zhang *et al.*, 2004; Haynes *et al.*, 2004) but absent in bis(guanidinium) 5-sulfosalicylate hydrate (Smith, Wermuth & Healy, 2004) and the quinolinium 5-sulfosalicylate structures (Smith, Wermuth & White, 2004). However, the common homomolecular cyclic $R_2^2(8)$ carboxylic acid association is found in both (II) and (III).

With the 5-SSA anion species in (I)–(III), structural and conformational features similar to those previously observed (Smith, Wermuth & White, 2004) are found. The usual intramolecular hydrogen bond is found between the phenol OH group and a carboxylate O atom [O2—H2···O72; O···O = 2.598 (3)–2.625 (2) Å], essentially giving coplanarity of the carboxylic acid group and the benzene ring [torsion angle C2—C1—C7—O71; 170.4 (2)–178.8 (3)°]. However, in only one compound, (I), is the carboxylic acid group involved in the strong single heteromolecular O—H···O(sulfonate) hydrogen-bonding interaction [2.632 (2) Å] found in most 5-SSA compounds. With (II) and (III), this group participates in the equally strong but cyclic homo-intermolecular interaction, while in none of the structures is there any intermolecular phenol O-atom participation.

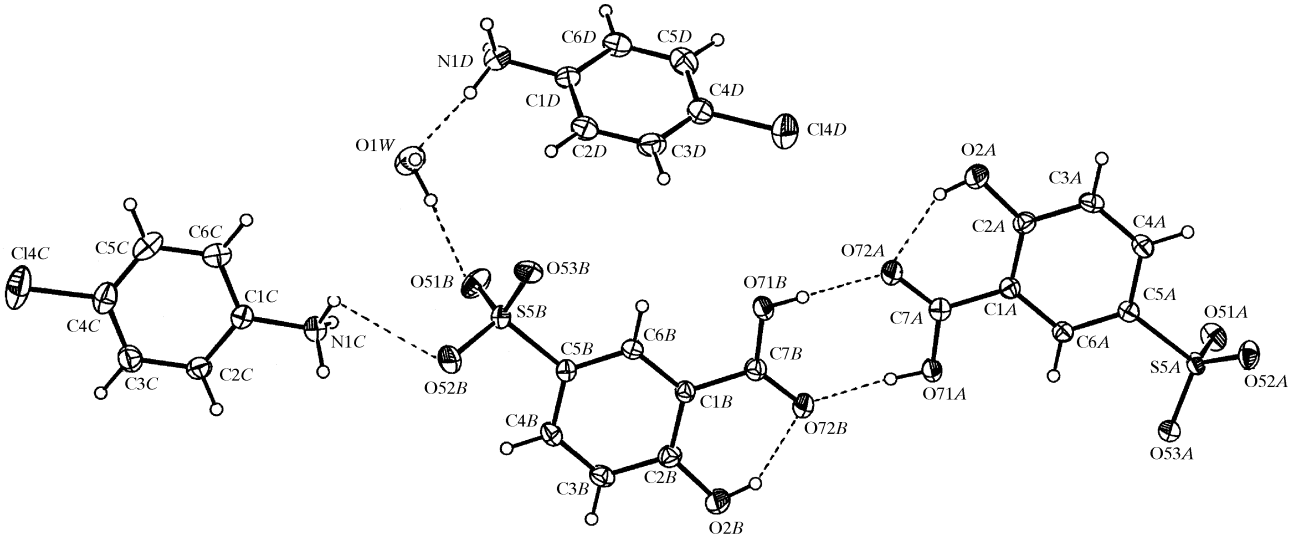


Figure 2
The atom-numbering scheme for the $CLAN^+$ cations (*C* and *D*), the $5\text{-}SSA^-$ anions (*A* and *B*) and the water molecule in (II). Non-H atoms are shown as 30% probability displacement ellipsoids.

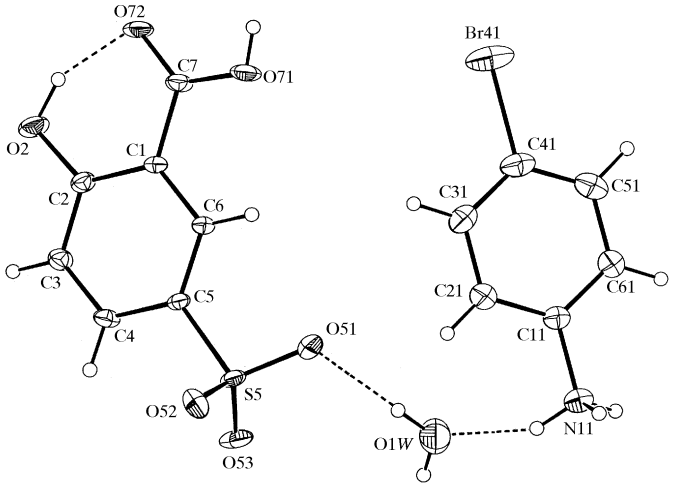


Figure 3
The molecular conformation and atom-numbering scheme for the $BRAN^+$ cation, the $5\text{-}SSA^-$ anion and the water molecule in (III). Non-H atoms are shown as 30% probability displacement ellipsoids.

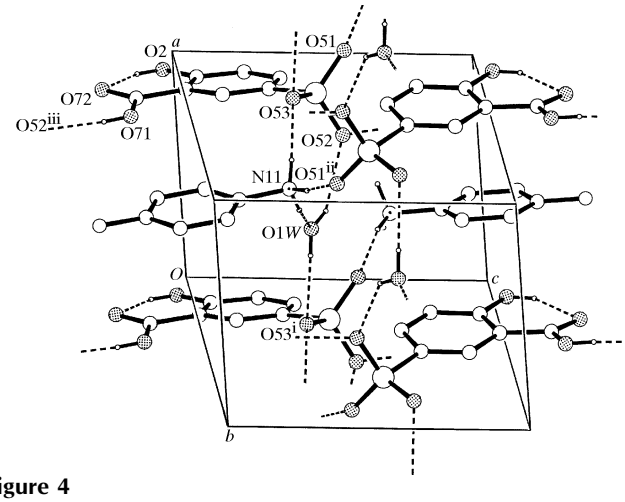


Figure 4
Structure extension through hydrogen-bonding interactions (shown as broken lines) in (I) in the unit cell viewed down the approximate *b* cell direction. H atoms not involved in hydrogen bonding have been omitted for clarity. For symmetry codes, see Table 1.

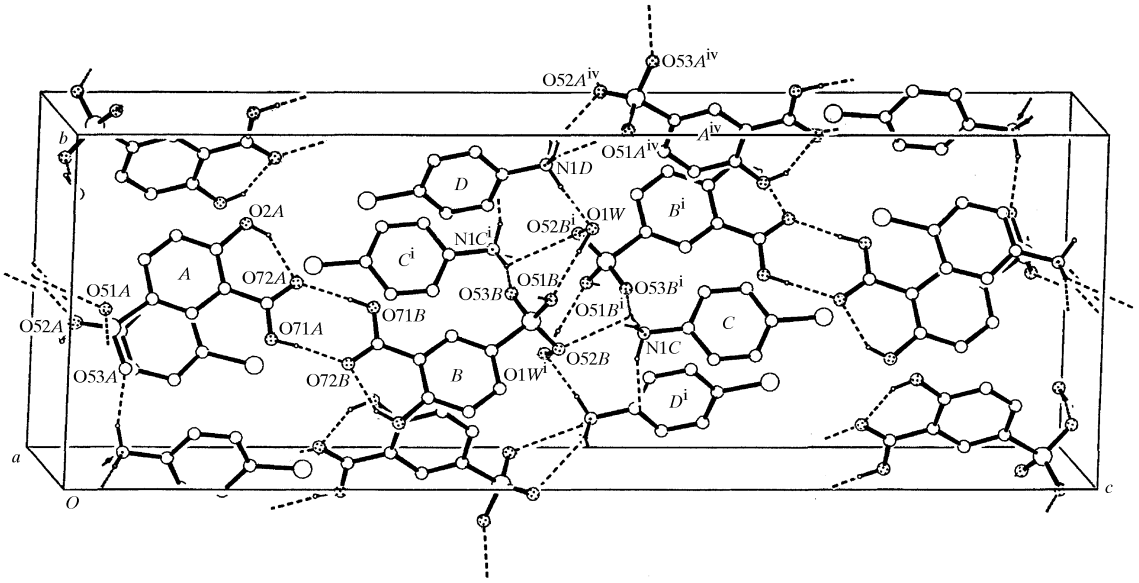


Figure 5
A perspective view of the hydrogen-bonding associations in (II) in the unit cell viewed down the approximate *a* cell direction. For symmetry codes, see Table 2.

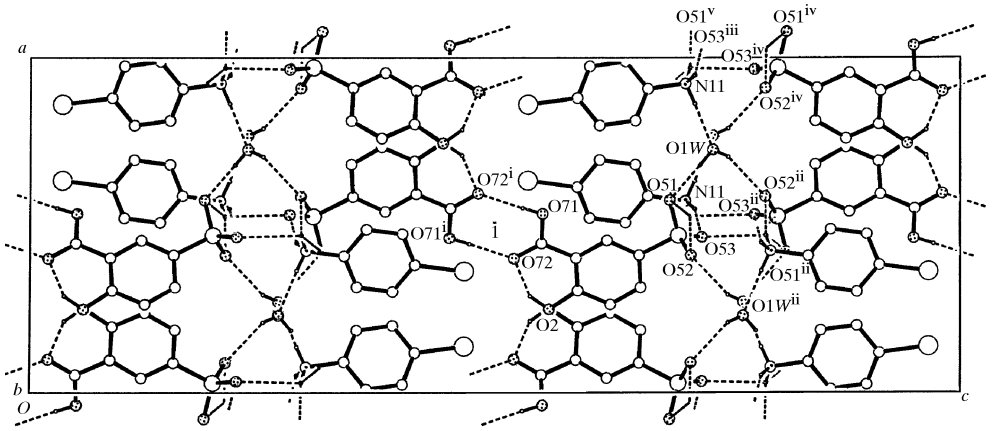


Figure 6
Hydrogen-bonding associations in (III) in the unit cell viewed down the *b* axis. For symmetry codes, see Table 3.

Compound (I) with 4-fluoroaniline (FAN^+·5-SSA^-·H_2O; Fig. 1) comprises layers of cation and anion pairs, which propagate along the 2_1 screw axis in the cell, linked by hydrogen-bonding interactions both within and between the layers (Table 2). The anilinium group is involved in three hydrogen-bonding interactions, two of which comprise direct N^+—H···O(sulfonate) links [N11···O53 and N11···O51^{ii}; symmetry codes for (I) are given in Table 1], the third being a link to the water molecule (N11···O1*W*). One of the water H atoms completes an unusual $R_3^3(8)$ cyclic association with a second sulfonate O atom (O1*W*···O52), while the second forms an interlayer bridge with another sulfonate O atom (O53^{i}). The result is that the water molecule effectively links together the cation/anion layers that form along the *a* cell direction. The carboxylic acid group of 5-SSA also gives a link along the *c* cell direction (O71···O52^{iii}), resulting in a three-dimensional hydrogen-bonded network structure (Fig. 4).

Although (II) is a hemihydrate, compounds (II), with 4-chloroaniline ($CLAN^+$·5-SSA^-·0.5H_2O), and (III), with 4-bromoaniline ($BRAN^+$·5-SSA^-·H_2O), are structurally similar. This similarity may be seen in Figs. 2, 3, 5 and 6. In both examples, the common $R_2^2(8)$ hydrogen-bonded cyclic carboxylic acid dimer is found, which in the case of (III) lies across a crystallographic inversion centre [O71···O72^{i} = 2.639 (3) Å; symmetry code: (i) $-x+1, -y+2, -z+1$], while in (II) the dimer is pseudo-centrosymmetric [O71*A*···O72*B* = 2.633 (3) Å and O71*B*···O72*A* = 2.634 (3) Å]. In both com-

pounds, the aminium H atoms form direct links to the sulfonate O-atom donors as well as to the water O atom [in (II), four for cation *C*, five for cation *D*; in (III), five in total; Tables 2 and 3]. The water molecule also acts as a bridging donor group in structure extension *via* the sulfonate groups. The result in both (II) and (III) is the formation of extensive hydrogen-bonded network polymeric structures. The structure of (II) contains some short non-bonding contacts between inversion-related sulfonate O atoms [O51*A*···O51*A*^{vii} = 2.815 (3) Å, O52*A*···O52*A*^{viii} = 2.875 (3) Å and O51*B*···O51*B*^{ix} = 3.071 (3) Å; symmetry codes: (vii) $-x, 1-y, -z$; (viii) $1-x, 1-y, -z$; (ix) $-x, 1-y, 1-z$].

Experimental

The title compounds were synthesized by heating under reflux for 10 min quantities (1 mmol) of 5-SSA and, respectively, 4-fluoroaniline (FAN), 4-chloroaniline (CLAN) and 4-bromoaniline (BRAN) in 50% ethanol/water (50 ml). After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solutions gave violet blocks of (I) (m.p. 517.0–518.5 K) and colourless flat prisms of (II) (m.p. 511.6–513.0 K) and (III) (m.p. 514.2–515.7 K).

Compound (I)

Crystal data

$C_6H_7FN^+\cdot C_7H_5O_6S^-\cdot H_2O$
M_r = 347.31
Monoclinic, $P2_1$
a = 6.7978 (7) Å
b = 12.5513 (12) Å
c = 8.5306 (8) Å
β = 96.529 (2)°
V = 723.12 (12) Å^3
Z = 2
D_x = 1.595 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2628 reflections
θ = 2.9–27.5°
μ = 0.27 mm^{-1}
T = 295 (2) K
Block, violet
0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
3741 measured reflections
2360 independent reflections
2275 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.0°
$h = -8 \rightarrow 7$
$k = -14 \rightarrow 14$
$l = -7 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.073
S = 1.03
2360 reflections
237 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), 1029 Friedel pairs
Flack parameter: 0.03 (3)

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O72	0.80 (3)	1.92 (4)	2.625 (2)	145 (4)
O1*W*—H1*A*···O53^{i}	0.83 (4)	2.19 (4)	3.019 (3)	177 (4)
O1*W*—H1*B*···O52	0.79 (5)	2.18 (4)	2.853 (3)	142 (4)
N11—H11*A*···O51^{ii}	0.89 (5)	2.01 (5)	2.882 (3)	168 (3)
N11—H11*B*···O53	0.88 (4)	2.03 (4)	2.910 (3)	172 (4)
N11—H11*C*···O1*W*	0.90 (3)	1.90 (4)	2.726 (3)	152 (4)
O71—H71···O52^{iii}	0.80 (4)	1.84 (4)	2.632 (2)	176 (4)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, y+\frac{1}{2}, -z+1$; (iii) $x, y, z-1$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O71*A*—H71*A*···O72*B*	0.83 (5)	1.80 (5)	2.633 (3)	175 (5)
O71*B*—H71*B*···O72*A*	0.81 (5)	1.83 (5)	2.634 (3)	172 (5)
O1*W*—H1*W*···O51*B*	0.90 (5)	1.92 (5)	2.815 (4)	180 (4)
O2*A*—H2*A*···O72*A*	0.81 (5)	1.90 (5)	2.607 (3)	145 (5)
O2*B*—H2*B*···O72*B*	0.82 (5)	1.89 (5)	2.608 (3)	145 (5)
O1*W*—H2*W*···O52*B*^{i}	0.96 (6)	1.96 (6)	2.920 (5)	175 (4)
N1*C*—H11*C*···O51*B*^{ii}	0.89 (5)	1.97 (5)	2.849 (4)	169 (5)
N1*D*—H11*D*···O52*A*^{iii}	0.87 (5)	2.14 (4)	2.845 (4)	137 (4)
N1*D*—H11*D*···O52*A*^{iv}	0.87 (5)	2.36 (5)	3.072 (3)	139 (4)
N1*C*—H12*C*···O53*A*^{v}	0.90 (5)	1.92 (5)	2.788 (3)	162 (5)
N1*D*—H12*D*···O1*W*	0.89 (5)	1.90 (5)	2.783 (4)	173 (4)
N1*C*—H13*C*···O53*B*^{i}	0.89 (5)	2.09 (5)	2.896 (4)	152 (5)
N1*C*—H13*C*···O52*B*	0.89 (5)	2.57 (5)	2.913 (4)	104 (5)
N1*D*—H13*D*···O51*A*^{vi}	0.88 (5)	1.94 (5)	2.810 (4)	168 (5)
N1*D*—H13*D*···O51*A*^{iv}	0.88 (5)	2.58 (5)	3.052 (3)	115 (4)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

Compound (II)

Crystal data

$C_6H_7ClN^+\cdot C_7H_5O_6S^-\cdot 0.5H_2O$
M_r = 354.77
Monoclinic, $P2_1/c$
a = 7.455 (4) Å
b = 11.849 (7) Å
c = 33.848 (19) Å
β = 90.817 (12)°
V = 2990 (3) Å^3
Z = 8
D_x = 1.576 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3985 reflections
θ = 2.4–27.6°
μ = 0.43 mm^{-1}
T = 295 (2) K
Block, colourless
0.45 × 0.30 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
11 861 measured reflections
5220 independent reflections
4133 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 10$
$l = -39 \rightarrow 40$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.132
S = 1.21
5220 reflections
444 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Compound (III)

Crystal data

$C_6H_7BrN^+\cdot C_7H_5O_6S^-\cdot H_2O$
M_r = 408.22
Orthorhombic, *Pbca*
a = 12.7810 (19) Å
b = 6.986 (1) Å
c = 35.454 (5) Å
V = 3165.6 (8) Å^3
Z = 8
D_x = 1.713 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4362 reflections
θ = 2.3–27.0°
μ = 2.76 mm^{-1}
T = 295 (2) K
Block, colourless
0.45 × 0.30 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.350, T_{max} = 0.436
14 778 measured reflections
2788 independent reflections
2203 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.0°
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 4$
$l = -42 \rightarrow 41$

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O72	0.84 (4)	1.84 (4)	2.598 (3)	149 (4)
O71—H72···O72^{i}	0.80 (4)	1.84 (4)	2.639 (3)	176 (3)
O1*W*—H1*A*···O52^{ii}	0.74 (6)	2.38 (6)	3.090 (5)	162 (5)
O1*W*—H1*B*···O51	0.84 (5)	1.99 (5)	2.827 (5)	179 (6)
N11—H11*A*···O53^{iii}	0.91 (3)	2.00 (3)	2.879 (3)	162 (3)
N11—H11*B*···O53^{iv}	0.89 (3)	2.53 (4)	2.897 (3)	106 (3)
N11—H11*B*···O51^{v}	0.89 (3)	2.56 (3)	3.081 (3)	119 (3)
N11—H11*B*···O52^{v}	0.89 (3)	2.22 (3)	3.100 (3)	172 (3)
N11—H11*C*···O1*W*	0.89 (4)	1.93 (4)	2.815 (5)	173 (3)

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, +y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{3}{2}, +y+\frac{1}{2}, z$; (iv) $+x+\frac{1}{2}, y, -z+\frac{3}{2}$; (v) $-x+\frac{3}{2}, +y-\frac{1}{2}, z$.

Table 4
Selected bond lengths and angles (Å, °) for (I), (II) and (III).

Data for the anion with atom-label suffix *A* and the cation with atom-label suffix *C* are in column three, and data for the anion with atom-label suffix *B* and the cation with atom-label suffix *D* are in column four.

	(I)	(II)*A*,*C*	(II)*B*,*D*	(III)
S5—O51	1.4535 (15)	1.453 (2)	1.456 (2)	1.448 (2)
S5—O52	1.4571 (15)	1.448 (2)	1.435 (2)	1.447 (2)
S5—O53	1.4599 (17)	1.439 (2)	1.446 (2)	1.452 (2)
S5—C5	1.768 (2)	1.769 (3)	1.767 (3)	1.768 (3)
F41—C41†	1.362 (3)	1.731 (3)	1.741 (3)	1.903 (3)
O2—C2	1.346 (3)	1.351 (3)	1.344 (3)	1.357 (3)
O71—C7	1.313 (3)	1.302 (3)	1.298 (3)	1.306 (3)
O72—C7	1.232 (3)	1.230 (3)	1.234 (3)	1.231 (3)
N11—C11	1.478 (3)	1.458 (3)	1.457 (3)	1.454 (4)
O51—S5—O52	111.52 (9)	112.68 (11)	111.85 (12)	111.44 (13)
O51—S5—O53	112.82 (10)	111.79 (13)	112.23 (12)	113.08 (12)
O51—S5—C5	107.24 (10)	103.74 (12)	105.25 (13)	106.76 (12)
O52—S5—O53	111.71 (11)	114.52 (12)	113.30 (13)	112.87 (12)
O52—S5—C5	106.76 (10)	106.37 (13)	106.68 (11)	106.13 (12)
O53—S5—C5	106.34 (10)	106.81 (11)	106.90 (12)	105.95 (12)
O2—C2—C1	122.7 (2)	123.2 (2)	123.2 (2)	123.4 (2)
O2—C2—C3	117.8 (2)	117.3 (2)	117.6 (2)	117.0 (2)
S5—C5—C6	120.63 (17)	120.7 (2)	119.19 (19)	121.2 (2)
S5—C5—C4	119.23 (19)	119.05 (18)	120.90 (18)	118.82 (19)
O72—C7—C1	122.9 (2)	122.1 (2)	121.9 (2)	121.4 (2)
O71—C7—O72	122.3 (2)	122.6 (2)	123.0 (2)	123.4 (3)
O71—C7—C1	114.8 (2)	115.2 (2)	115.0 (2)	115.2 (2)
N11—C11—C61	119.7 (2)	120.3 (2)	119.4 (2)	119.1 (2)
N11—C11—C21	118.4 (2)	118.9 (2)	120.2 (2)	120.5 (3)
F41—C41—C31	118.9 (2)	119.2 (2)	119.4 (3)	119.6 (3)
F41—C41—C51	118.1 (2)	119.8 (3)	119.3 (2)	119.2 (3)
O51—S5—C5—C4	51.89 (19)	−73.8 (3)	−84.0 (2)	169.1 (2)
O52—S5—C5—C4	−67.76 (19)	45.3 (3)	35.0 (3)	−71.9 (2)
O53—S5—C5—C4	172.84 (17)	168.0 (2)	156.5 (2)	48.3 (3)
O51—S5—C5—C6	−126.64 (18)	98.9 (2)	96.9 (2)	−15.0 (3)
O52—S5—C5—C6	113.71 (18)	−142.0 (2)	−144.1 (2)	103.9 (2)
O53—S5—C5—C6	−5.7 (2)	−19.3 (3)	−22.6 (3)	−135.8 (2)
C2—C1—C7—O71	170.4 (2)	176.0 (3)	178.8 (3)	177.2 (2)
C6—C1—C7—O71	−8.8 (3)	−2.7 (4)	−1.9 (4)	0.0 (4)
C6—C1—C7—O72	172.4 (2)	177.7 (3)	179.1 (3)	179.9 (2)
C2—C1—C7—O72	−8.5 (3)	−3.6 (4)	−0.2 (4)	−3.0 (4)

† For F41 read Cl4*C*, Cl4*D* and Br41 in columns 3, 4 and 5, respectively.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.112$
$S = 1.07$
2842 reflections
237 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.9744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

H atoms involved in hydrogen-bonding interactions (anilinium, carboxyl, phenol and water) were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the respective refinements at calculated positions (C—H = 0.93 Å) and allowed for as riding [with $U_{iso}(H) = 1.2U_{eq}(C)$].

For all three compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999) data reduction: *SAINT*; structure solution: *SHELXTL* (Bruker, 1997); structure refinement: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); publication software: *PLATON*.

The authors acknowledge financial support from The School of Physical and Chemical Sciences of the Queensland University of Technology and The University of Melbourne.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1595). Services for accessing these data are described at the back of the journal.

References

Bakasova, Z. B., Abdybaliev, D. A., Sharipov, Kh. T., Akbaev, A. A., Ibragimov, B. T., Talipov, S. A. & Ismankulov, A. I. (1991). *Uzb. Khim. Zh.* pp. 22–25.

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SADABS* (Version 2.03) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Haynes, D. A., Chisholm, J. A., Jones, W. & Motherwell, W. D. S. (2004). *CrystEngComm*, **6**, 584–588.

Madarasz, J., Bombicz, P., Jarmi, K., Ban, M., Pokol, G. & Gal, S. (2002). *J. Therm. Anal. Calorim.* **69**, 281–290.

Muthiah, P. T., Hemamalini, M., Bocelli, G. & Cantoni, A. (2003). *Acta Cryst.* E**59**, o2015–o2017.

Raj, S. B., Sethuraman, V., Francis, S., Hemamalini, M., Muthiah, P. T., Bocelli, G., Cantoni, A., Rychlewska, U. & Warzajtis, B. (2003). *CrystEngComm*, **5**, 70–76.

Russell, V. A., Etter, M. C. & Ward, M. D. (1994). *J. Am. Chem. Soc.* **116**, 1941–1952.

Smith, G., Wermuth, U. D. & Healy, P. C. (2004). *Acta Cryst.* E**60**, o687–o689.

Smith, G., Wermuth, U. D. & White, J. M. (2004). *Acta Cryst.* C**60**, o575–o581.

Spek, A. L. (2003). *J Appl. Cryst.* **36**, 7–13.

Zhang, X.-L., Chen, X.-M. & Ng, S. W. (2004). *Acta Cryst.* E**60**, o453–o454.